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TECHNICAL REPORT ARSCD-TR-83007

CORROSION SUSCEPTIBILITIES OF MAGNESIUM ALLOYS AZ91, EZ33 AND ZE41

ANTHONY GALLACCIO
WILLIAM T. EBIHARA

JUNE 1983

US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
FIRE CONTROL AND SMALL CALIBER
WEAPON SYSTEMS LABORATORY
DOVER, NEW JERSEY

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An assessment was made of the corrosion susceptibility of cast magnesium alloys AZ91C-T6, EZ33A-T5 and ZE41A-T5. Efforts were made to establish the influence of as-cast and machined surfaces on the corrosion behavior. Cast test panels of AZ91C-T6 alloy were compared with specimens obtained from an AZ91C-T6 helicopter transmission gear housing. The corrosion rates were derived by measuring the hydrogen gas evolved by specimens immersed in sodium chloride solution. The relative order of corrosion susceptibility for panel specimens was:

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20. ABSTRACT (Cont)

AZ91C-T6 > EZ33A-T5 > ZE41A-T5. AZ91C-T6 gear housing specimens exhibited the lowest corrosion rates. The lower corrosion behavior of housing material was attributed to its relatively uniform microstructure, compositional homogeneity and low level of porosity. The effect of micropores on corrosion behavior was thought to mask the influences attributed to surface condition for the test panels.

FOREWORD

This report, the second issued under the project (PRON EJ4H00-4200 EJF6), treats the inherent corrosion behavior of cast magnesium alloys, AZ91C-T6, EZ33A-T5 and ZE41A-T5.

The first report (ref 1), based on another phase of the project, presented an analysis of effects of surface processings or treatments and of protective coatings including anodic coatings on the fatigue strength of the alloys. A third report concerning the effect of the addition of corrosion inhibiting agents to mineral and synthetic lubricating oils (ref 2) on the corrosion resistance of DOW 7 treated magnesium alloys will be forthcoming.

CONTENTS

	Page
Introduction	1
Experimental	2
Materials	2
Specimens	2
Apparatus	2
Procedure	3
Results and Discussion	3
Results	3
AZ91 Panels	4
EZ33 Panels	4
ZE41 Panels	4
AZ91 Housing	4
Discussion of Results	5
Conclusions	6
References	7
Distribution List	25

TABLES

		Page
1	Alloy designations and composition	9
2	Corrosion test results of magnesium alloys in sodium chloride solution	10

FIGURES

1	Pattern of specimens, 1 x 2 cm, taken from panels 9.5 x 10.2 x 15.2 cm for measurements of H_2 evolution	11
2	Helicopter gear box housing (0.185 x mag.) - large numbers refer to position of strip (5.7 x 20.3 cm), smaller numbers in strip show position of specimen (1 x 2 cm)	12
3	Helicopter gear box housing - strip positions 2, 3, and 4	13
4	Helicopter gear box housing - strip positions 5 through 9	14
5	Detail of specimen for hydrogen evloution measurements	15
6	Apparatus for collecting and measuring hydrogen evolved by a magnesium specimen in sodium chloride solution	16
7	Hydrogen evolution, AZ91C-T6 as-cast, panel B	17
8	Hydrogen evolution, AZ91C-T6 machined, panel B	18
9	Hydrogen evolution, EZ33A-T5 as-cast, panel B	19
10	Hydrogen evolution, EZ33A-T5 machined, panel B	20
11	Hydrogen evolution, ZE41A-T5 as-cast, panel B	21
12	Hydrogen evolution, ZE41A-T5 machined, panel B	22
13	Hydrogen evolution, AZ91C-T6 housing as-cast	23
14	Hydrogen evolution, AZ91C-T6 housing machined	24

INTRODUCTION

Magnesium alloys have decided advantages in some structural engineering applications. Their high strength-to-weight characteristics relative to other structural metals make them very desirable to use in aircraft, rockets, and space equipment. Some magnesium alloys possess excellent stiffness-to-weight properties. However, since magnesium alloys are chemically more reactive than other structural metals, emphasis must be placed on the efficacy and care of protective systems applied to these alloys. Unquestionably, this consideration applies to cast or wrought magnesium components of aircraft, which encounter a wide range of environmental conditions, such as airborne salts, high humidity, moisture, liquid fuels, oils, and cleaning compounds. On helicopters, physical damage to the protective film is likely to result from impact of grit or small stones lifted by rotor-caused air turbulence, leading to vulnerability to corrosion of the exposed magnesium.

More extensive use of magnesium alloys would be realized if significantly better protection from corrosion could be assured (ref 3). At the present stage of the magnesium protection technology, effective coating systems are available but need to be optimized for use (ref 4).

Toward this optimization, several dependent influences should be investigated. First, there is a possible effect on fatigue strength of a magnesium alloy associated with anodizing the surface. The thicker anodic coatings provide a superior protective base for a subsequent organic finish, but have been claimed (refs 5 and 6) to cause reduction of fatigue strength. The findings in the first report of this study (ref 1) demonstrate that anodic coatings are not necessarily detrimental to fatigue strength and identifies acid pickling as the major cause in fatigue strength reduction.

Second, since the corrosion of magnesium is markedly accelerated if galvanically coupled to dissimilar metals, (refs 7 and 8) practical means for precluding galvanic corrosion involving materials and techniques are dictated. Third, the selection of an effective corrosion resistant organic coating should take into consideration good adherence to the underlying surface, reasonable toughness and flexibility, excellent corrosion resistance to liquids fuels and lubricants, and easy repairability.

This reported work effort is directed to the expressed needs of the Troop Support and Aviation Materiel Readiness Command (TSARCOM) and the Aviation Research and Development Command (AVRADCOM) concerning cast magnesium alloy helicopter gear housings. For this work, the magnesium alloys AZ91C-T6, EZ33A-T5 and ZE41A-T5 were chosen as candidate materials. Helicopter gear housings in service are AZ91C-T6 alloy. These are chromated (Dow 7) overall and are finished externally with a chromate primer, followed by an acrylic lacquer; internally, an epoxy resin coating is applied over the Dow 7 pretreatment. The EZ33 and ZE41 alloys are of interest to TSARCOM/AVRADCOM, because of their reported lower susceptibility to general corrosion and better weldability, which is of importance for easier repair of castings.

EXPERIMENTAL

Materials

Cast panels of magnesium alloys AZ91, EZ33 and ZE41 and a cast helicopter transmission gear housing of AZ91 were evaluated in this study. The designation and nominal composition of each material are given in table 1.

Cast panels of each alloy representing three different heats were procured from Hitchcock Industries, Inc. Foundry Division, Minneapolis, MN. These measured 10.16 x 15.24 x 0.95 cm (4 x 6 x 0.39 in), and were treated with Dow 1. A helicopter housing, which was in service for about four years (no other information was available) was obtained from Corpus Christi Army Depot (CCAD) for evaluation.

Specimens

Specimens (1 x 2 cm) were cut from three panels of each alloy (each panel representing different heat) and from strips removed from the helicopter housing, as mapped in figures 1 through 4. Panel specimens with the original as-cast top and bottom surfaces, but with machined edges and sides, and specimens from the helicopter housing with one (external as-cast surface, are referred to herein as as-cast specimens. Other specimens from panels or housing strips, were machined and abraded to remove the as-cast surfaces. These are referred to as machined specimens. These were prepared to compare corrosion of as-cast and machined specimens from the same panel. The as-cast specimens were 0.95-cm thick. The machined specimens were 0.90-cm thick since approximately 0.025 cm was removed from each surface.

Cast surfaces were removed with abrasive papers, 80 grit aluminum oxide (Al_2O_3) followed by 600 mesh silicon carbide (SiC) then rubbed with Scotch-Brite,* type S. Cut and machined surfaces were rubbed with the SiC paper, followed with Scotch-Brite.

A 0.2 cm diameter hole was drilled in all specimens to accomodate a thin chromel (B&S 26) wire hook to suspend the coupon during the measurements (figure 5).

Apparatus

After the specimens had been abraded, they were cleaned in a liter solution of sodium orthosilicate (60g/l) with an addition of 3g Nacconal 4 at about 30°C (86°F). A reaction flask, eudiometer and auxillary components were arranged, as shown in figure 6, to collect hydrogen evolved by the magnesium specimens. The corrosion medium was neutral 5 percent sodium chloride solution. A new 500-ml solution was used for each determination. A magnetic stirrer was added so that the solution could be agitated continuously during the determination to preclude buildup of magnesium ions at the specimen surface. Four apparatuses were operated simultaneously and tests were conducted within an eight hour shift.

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*Trademark, product of 3M Company, Minneapolis, MN.

Procedure

Prior to initiating a run, the specimen was cleaned in the alkaline cleaning solution, rinsed with distilled water, then rinsed with acetone, and finally dried in air. A small wire hook of chromel (B&S 26) was fastened through the drilled hole. The hook was used to fasten a dacron filament (about 17 cm in length), to position the specimen to about half-depth in the solution. At the beginning of each run, and immediately on immersing the specimen, the internal pressure was adjusted to atmospheric pressure and all valves positioned to allow hydrogen gas to be collected. Temperature and pressure were noted at the outset and the volume of gas evolved was noted periodically over a period of seven hours. On completing the determination and adjusting the internal pressure to that of the atmosphere, the collected volume was measured. Adjustments were made for temperature, water vapor and barometric pressure to standardize the volumetric data.

The amount of hydrogen collected is directly related to the amount of magnesium dissolved. The overall equation for the corrosion reaction is as follows:

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$$

Therefore, each hydrogen molecule collected represents one atom of magnesium dissolved. Thus, the corrosion rate in terms of $mg/dm^2/day$ for magnesium is:

$$C.R. = \frac{VR}{SA.t}$$

C.R. = corrosion rate

where V = ml of hydrogen collected at standard temperature and pressure (STP)

R = atomic wt mg/molecular volume H_2 = 1086 mg/ml

SA = surface area of specimen in dm^2

t = time interval in days

One of the objectives of this work was to assess the corrosion susceptibility of as-cast versus machined surfaces. Therefore, corrosion rates as-cast and machined specimens from the same source (panel or housing strip) were compared.

RESULTS AND DISCUSSION

Results

The results of the hydrogen evolution tests are given in table 2. The reduced data presented were obtained utilizing computerized plotting and linear-least squares analyses. The evolution rate is the average slope obtained from the linear least-squares analysis along with variance computed for each set of data. Representative graphical plots for each alloy, as-cast and machined are shown in figures 7 to 14.

AZ91 Panels

As shown in table 2, as-cast specimens of panel A exhibited an extremely high average corrosion rate of 6138 mg/dm^2/day compared with rates of 1318 to 2021 mg/dm^2/day for as-cast specimens of B and C panels, respectively. Fairly high variances, especially for A and B panels (figures 7 and 8), are also noted.

The machined AZ91C-T6 specimens also exhibited considerable variance but showed fairly consistent corrosion rate averages, i.e., 1442 to 1746 mg/dm^2/day. These averages are within the range exhibited for the as-cast specimens (panels B and C). Thus, the corrosion behavior is not significantly different between the as-cast and the machined specimens.

EZ33 Panels

The plots of corrosion data obtained for as-cast and machined specimens of panel B (figures 9 and 10, respectively) are typical for all the panels regardless of surface condition. The average corrosion rate for the as-cast panels ranged from 895 to 1188 mg/dm^2/day and for the machined panels, from 1033 to 1048 mg/dm^2/day. Again, other than the greater consistency observed for the corrosion of machined specimens, marked differences in corrosion rate between the two surface conditions could not be found. The average corrosion rate for the EZ33 alloy specimens was lower that that observed for the AZ91 alloy specimens.

ZE41 Panels

The corrosion behavior of ZE41A-T5 alloy specimens, regardless of surface condition, appeared to be quite consistent (figures 11 and 12). The as-cast specimens exhibited corrosion rates from 535 to 742 mg/dm^2/day while rates from the machined specimens ranged from 625 to 710 mg/dm^2/day. Again, marked differences in corrsion behavior of the as-cast and machined specimens were not discernible. The corrosion rates for the ZE41 panels were lower than that for EZ33 alloy panels and approximately one-half that exhibited by AZ91 alloy panels.

AZ91 Housing

The corrosion behavior observed for the helicopter housing specimens is displayed in figures 13 and 14 for the as-cast and machined surface conditions, respectively. Compared with the AZ91 alloy panel results, markedly lower rates, as well as low scatter of data, were exhibited by the AZ91 housing specimens. Specifically, the rates observed for the machined housing specimens were approximately one-fourth that exhibited by machined AZ91 panels. Also, the machined housing specimens exhibited a significantly lower corrosion rate (361 mg/dm^2/day), as well as extremely low data point scatter, compared with the as-cast housing specimens (594 mg/dm^2/day). The other observation is that the corrosion rate exhibited by the housing specimens was also lower that that observed for the EZ33 and ZE41 alloy panels. The exception to this general observation is that the as-cast ZE41 panel A specimens exhibited slightly lower corrosion rate compared with rate for the as-cast AZ91 housing specimens.

Discussion of Results

There are several noteworthy observations in the corrosion test results. These are as follows:

- Considerable scatter of data points was observed for AZ91C-T6 panel specimens.
- The average corrosion rate for as-cast panel A AZ91 specimens was considerably higher than that observed for machined panel A specimens.
- With the exception of AZ91 panel A and the housing specimens, differences in corrosion behavior between as-cast and machined surfaces are marginal.
- A significant difference is noted in the corrosion behavior of cast AZ91 panel and cast AZ91 housing specimens.
- The corrosion rate of machined AZ91 housing specimens is lower than that for ZE41, EZ33 and AZ91 panel specimens.

The erratic corrosion behavior noted (especially for the AZ91 alloy panel specimens) can be attributed to a number of possible factors including microstructural and compositional inhomogeneity, grain size, grain morphology and microporosity. Aside from microporosity, the other factors were beyond the scope of consideration of this project. However, as a part of this project, Fiore (ref 9) showed that there was a definite correlation between the micropore density and the observed corrosion rate for AZ91C-T6 alloy specimens. He observed that corrosion either proceeded by uniform attack on the metal surface or by preferential attack at micropores located at the interdendritic regions. The overall corrosion rate was observed to be a function of the amount of porosity on the exposed surfaces. While these observations do not conclusively prove that micropores are solely responsible for the observed erratic and enhanced corrosion behavior, they do strongly suggest that microporosity plays a key role in the corrosion process. Other factors, such as phase distribution and compositional inhomogeneity, cannot be disregarded as posible influences.

These factors must be considered in interpreting the results observed for the AZ91C-T6 panel A specimens, i.e., the corrosion rate exhibited by the as-cast panel A specimens was approximately 3.5 times that observed for machined specimens from panel A. Surface porosity could contribute somewhat but phase or compositional inhomogeneity in the surface layer's region are likely factors for the enhanced corrosion behavior observed for the as-cast A panel specimens since machined specimens from the same lot exhibited considerably lower corrosion rates.

The removal of the surface layers resulted in more consistent corrosion behavior for all the alloys tested. However, unlike AZ91 panel A specimens, the machined surfaces did not reveal significant reductions or differences in corrosion behavior for alloys EZ33 and ZE41. The inhomogeneities in the surface layers could be eliminated by the machining process but micropores would still exist. The machining action will smear material over the pores but as the corrosion process proceeds, the pores would be exposed in a relatively short time period (ref 9). Thus, the uniformity or consistency of results observed for the

machined specimens appears to be the result of removing the surface regions which may differ with the interior regions in terms of microstructure and composition. The lack of significant differences in the corrosion behavior of as-cast and machined specimens is probably due to the overriding effect of micropores on corrosion.

The differences in corrosion behavior observed between the AZ91 panel specimens and the housing specimens can be attributed to all the aforementioned factors. However, considering the observation that the corrosion rate for the AZ91 housing was lower than that of ZE41 or EZ33 alloy panel specimens, factors other than phase or compositional inhomogeneities must be addressed. The presence of micropores is more likely to occur in thin sections, as with the panel material, rather than with the more massive castings where the solidification rate is slower and more controlled. The presence of micropores, as discussed earlier, will cause preferential or enhanced corrosion and its observed presence in the panel specimens could explain the higher rate observed for the AZ91 panels compared to the AZ91 housing specimens. The presence of micropores in the EZ33 and ZE41 panel specimens could also explain the observation that the corrosion rates for these specimens was higher than that observed for the housing specimens.

Finally, the corrosion behavior differences between the as-cast housing specimens and the machined AZ91 housing specimens must be considered. The amount of data point scatter for the as-cast specimens is approximately twice that observed for the machined specimens. This indicates considerably more metallurgical or chemical variablity in the as-cast material compared to the machined specimens. Further, the machined housing specimens required considerably more material removal than the machined panel specimens owing to the original thicker cross section of the housing. Thus, the likelihood of uniform material is greater with the machined housing specimens than with the as-cast specimens. Consequently, it is likely that the lower corrosion behavior observed for the machined specimens is due to the removal of structural and compositional inhomogeneities.

CONCLUSIONS

1. The order of corrosion susceptibility of the alloy panel castings is:

AZ91C-T6 > EZ33A-T5 > ZE41A-T5

2. The thin, cast AZ91 panels are more susceptible to corrosion than the same alloy as a cast housing. The greater inhomogeneity of the microstructure (with microporosity as a key factor) of the panels is likely to be a major reason for this observation.

3. The lower corrosion rate and the low amount of data point scatter observed for the AZ91 housing material can be attributed to a more uniform microstructure with a lower level of microporosity due to a more controlled solidification of casting process compared with that for producing thin cast panels.

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Table 1. Alloy designations and composition

Designation	Form	Constituents (wt%)					
		Al	Zn	Mn	Zr	Ce	Mg
AZ91C-T6[a]	Panel	8.75	0.81	0.13	-	-	Bal.
EZ33A-T5[b]	Panel	-	2.75	-	0.68	2.94	Bal.
ZE41A-T5[b]	Panel	-	3.71	-	0.89	1.44	Bal.

[a]T6 - Solution heat treated and thermally aged

[b]T5 - Thermally aged

Table 2. Corrosion test results of magnesium alloys in sodium chloride solution

Alloy	Panel	Surface Condition	Number Tested	Evolution Rate (ml/hr)	Variance (ml/hr)	Corrosion Rate (mg/dm^2/d)	Variance (mg/dm^2/d)
AZ91C-T6	A	as cast	13	22.135	1.309	6138	363
"	B	as cast	13	7.288	1.341	2021	372
"	C	as cast	13	4.752	0.378	1318	105
"	A	machined	12	6.297	1.445	1746	401
"	B	machined	12	5.200	1.262	1442	350
"	C	machined	12	5.615	1.306	1556	362
EZ33A-T5	A	as cast	12	3.228	0.405	895	112
"	B	as cast	13	3.230	0.254	896	70
"	C	as cast	13	4.283	0.986	1188	273
"	A	machined	11	3.778	0.439	1048	122
"	B	machined	10	3.761	0.348	1043	96
"	C	machined	11	3.726	0.438	1033	121
ZE41A-T5	A	as cast	13	1.930	0.183	535	51
"	B	as cast	13	2.677	0.204	742	57
"	C	as cast	13	2.415	0.283	670	78
"	A	machined	11	2.255	0.355	625	98
"	B	machined	11	2.560	0.226	710	63
"	C	machined	12	2.323	0.221	644	61
AZ91C-T6	housing	as cast	25	2.143	0.232	594	64
"	housing	machined	26	1.303	0.119	361	33

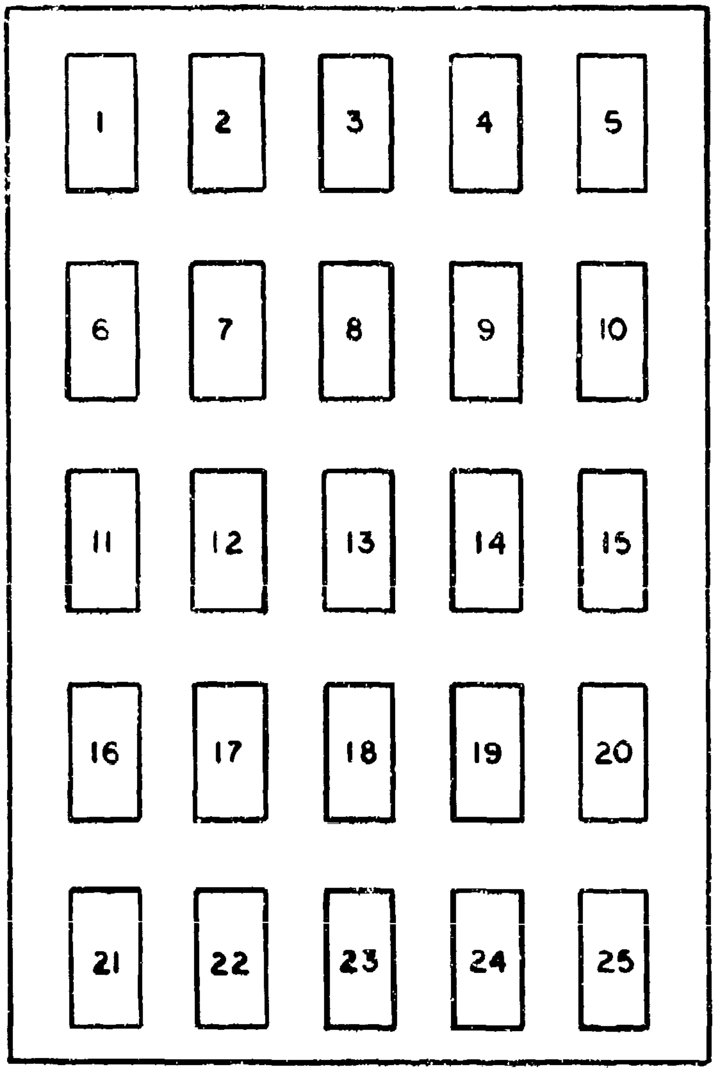

Figure 1. Pattern of specimens, 1 x 2 cm, taken from panels 9.5 x 10.2 x 15.2 cm for measurements of H_2 evolution

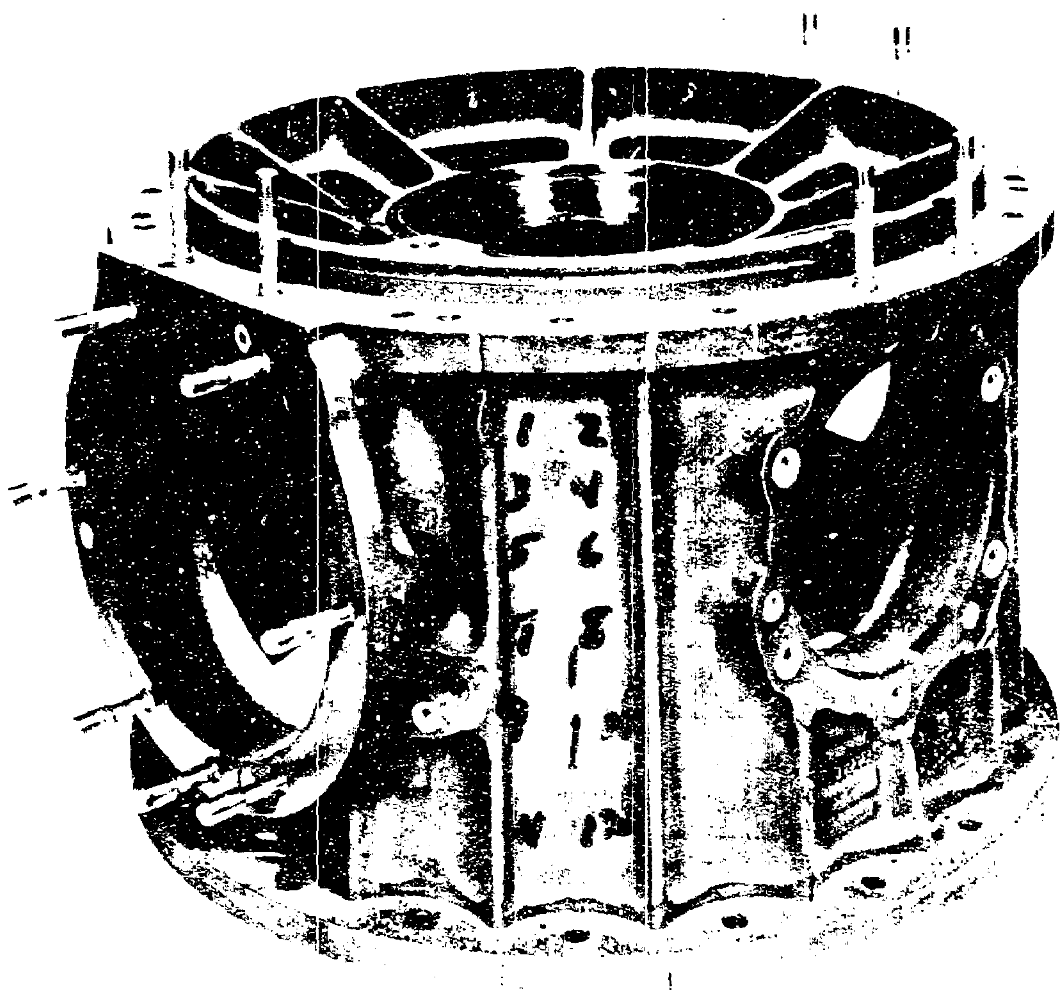

Figure 2. Helicopter gear box housing (0.185 x mag.) - large numbers refer to position of strip (5.7 x 20.3 cm), smaller numbers in strip show position of specimen (1 x 2 cm)

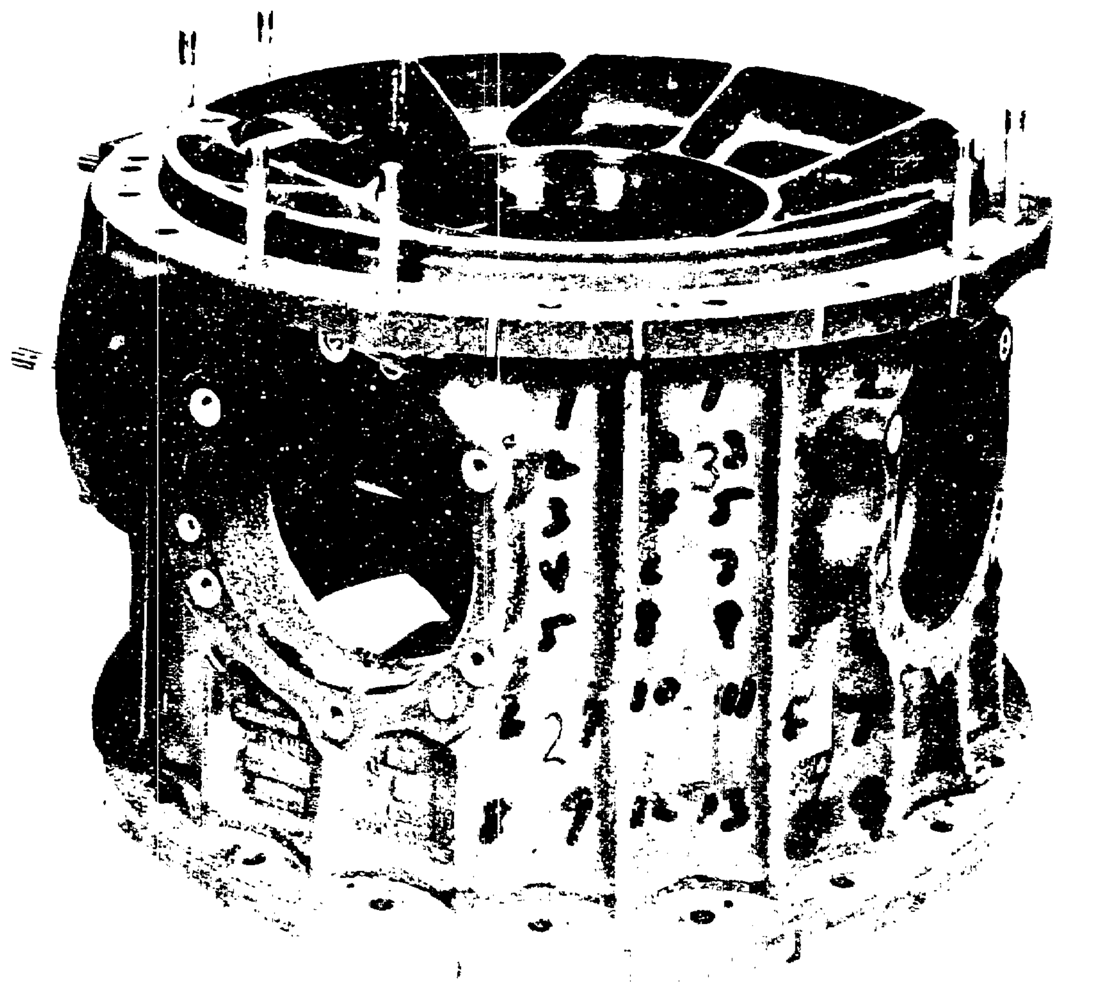

Figure 3. Helicopter gear box housing - strip positions 2, 3, and 4

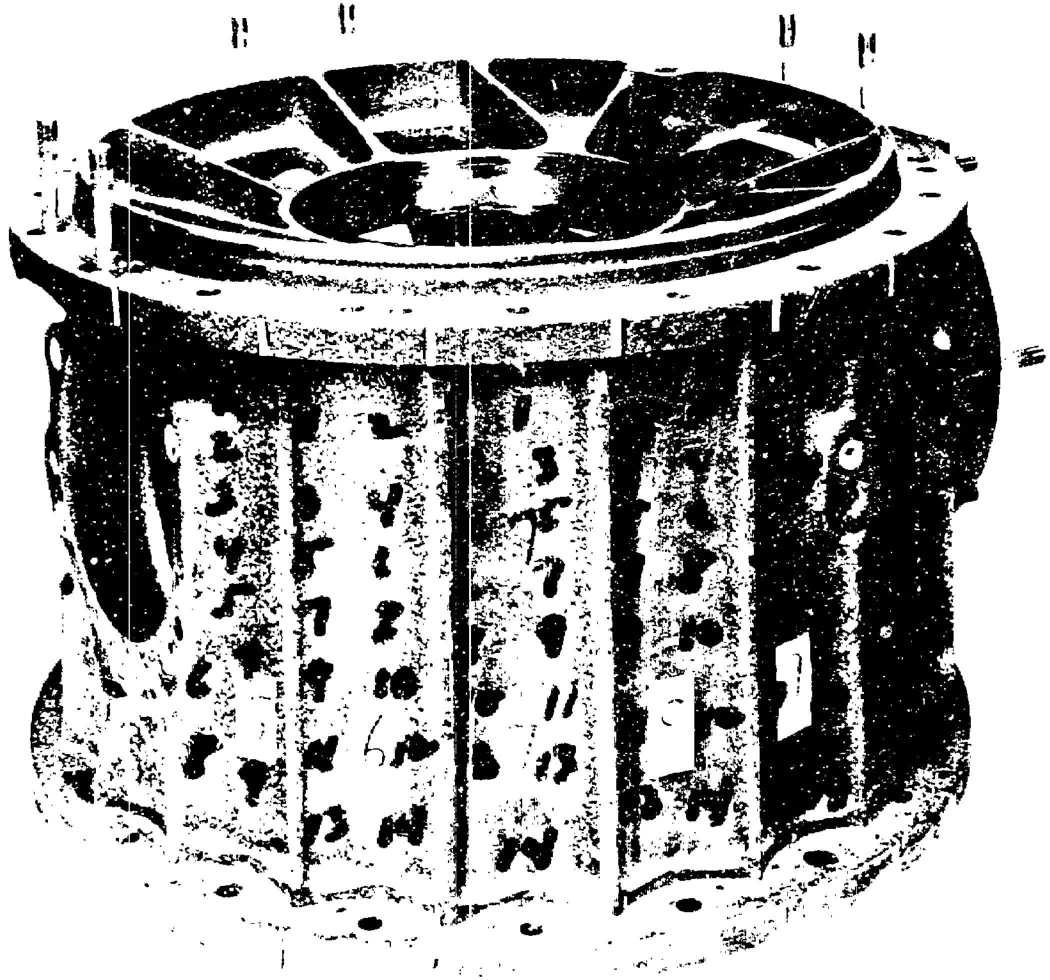

Figure 4. Helicopter gear box housing - strip positions 5 through 9

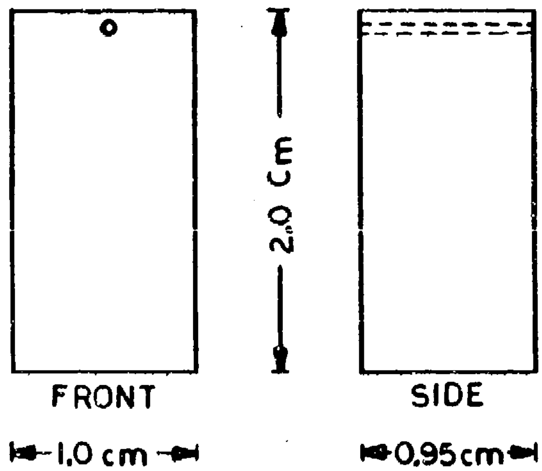

Figure 5. Detail of specimen for hydrogen evolution measurements

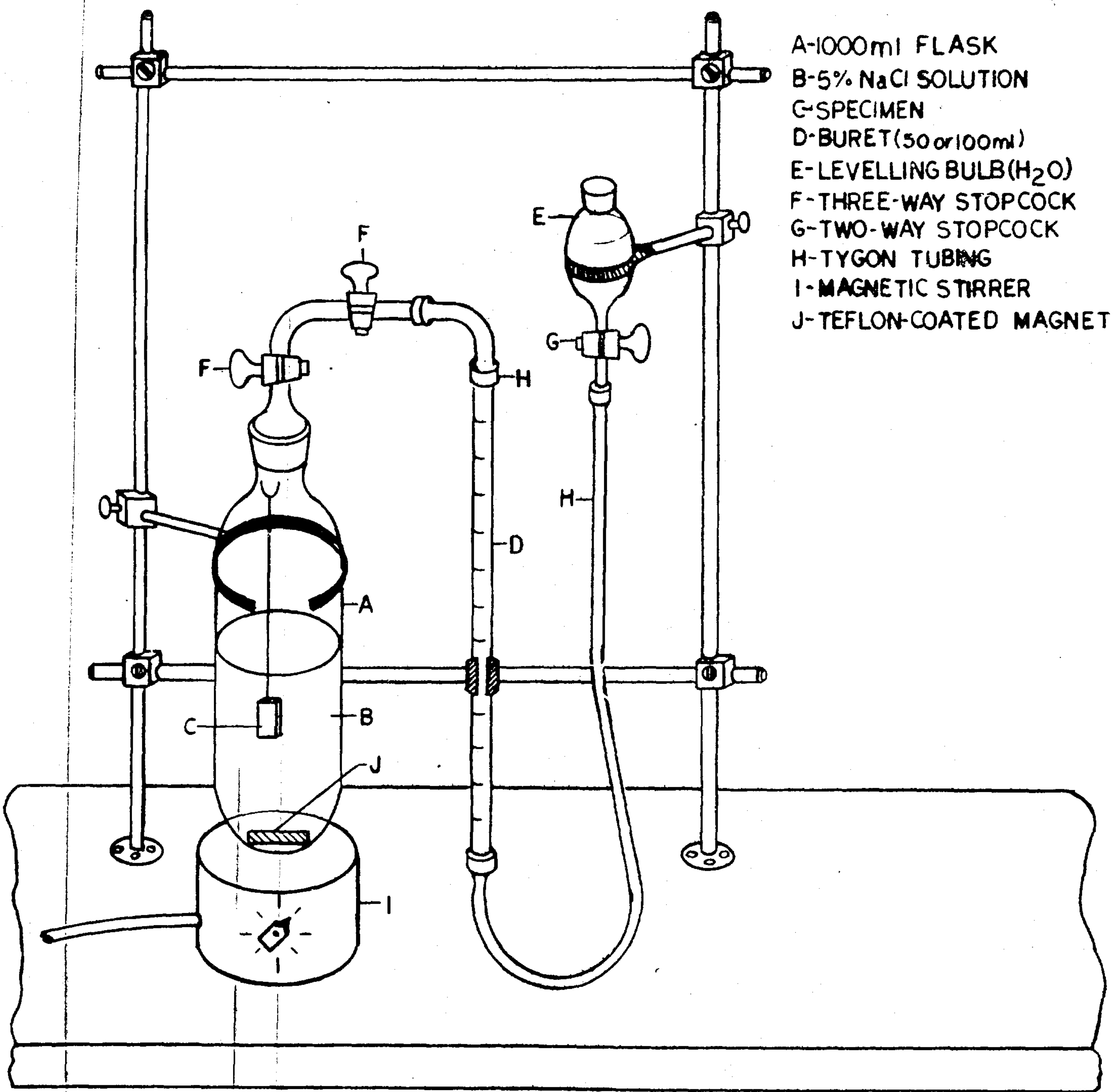

Figure 6. Apparatus for collecting and measuring hydrogen evolved by a magnesium specimen in sodium chloride solution

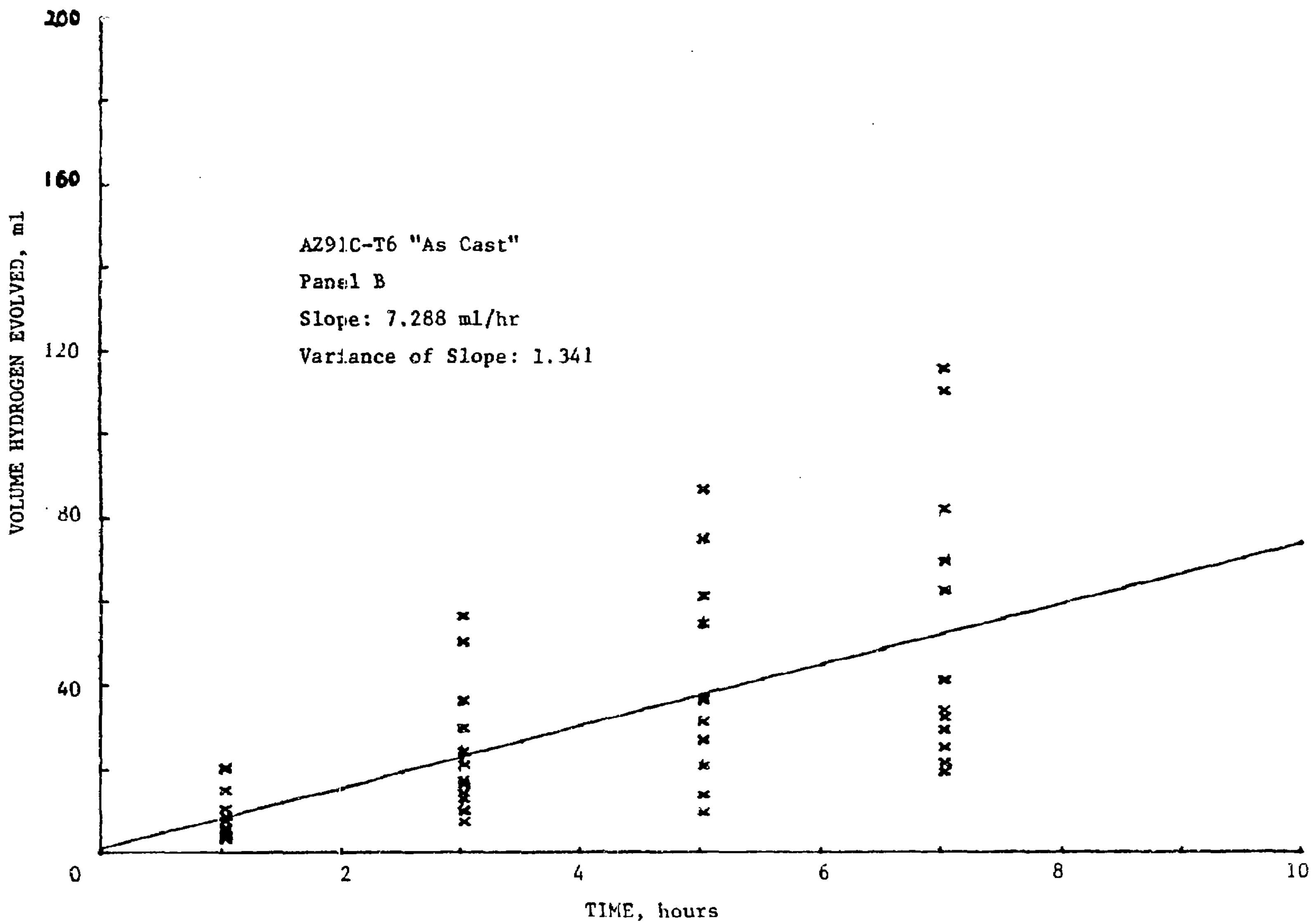

Figure 7. Hydrogen evolution, AZ91C-T6 as-cast, panel B

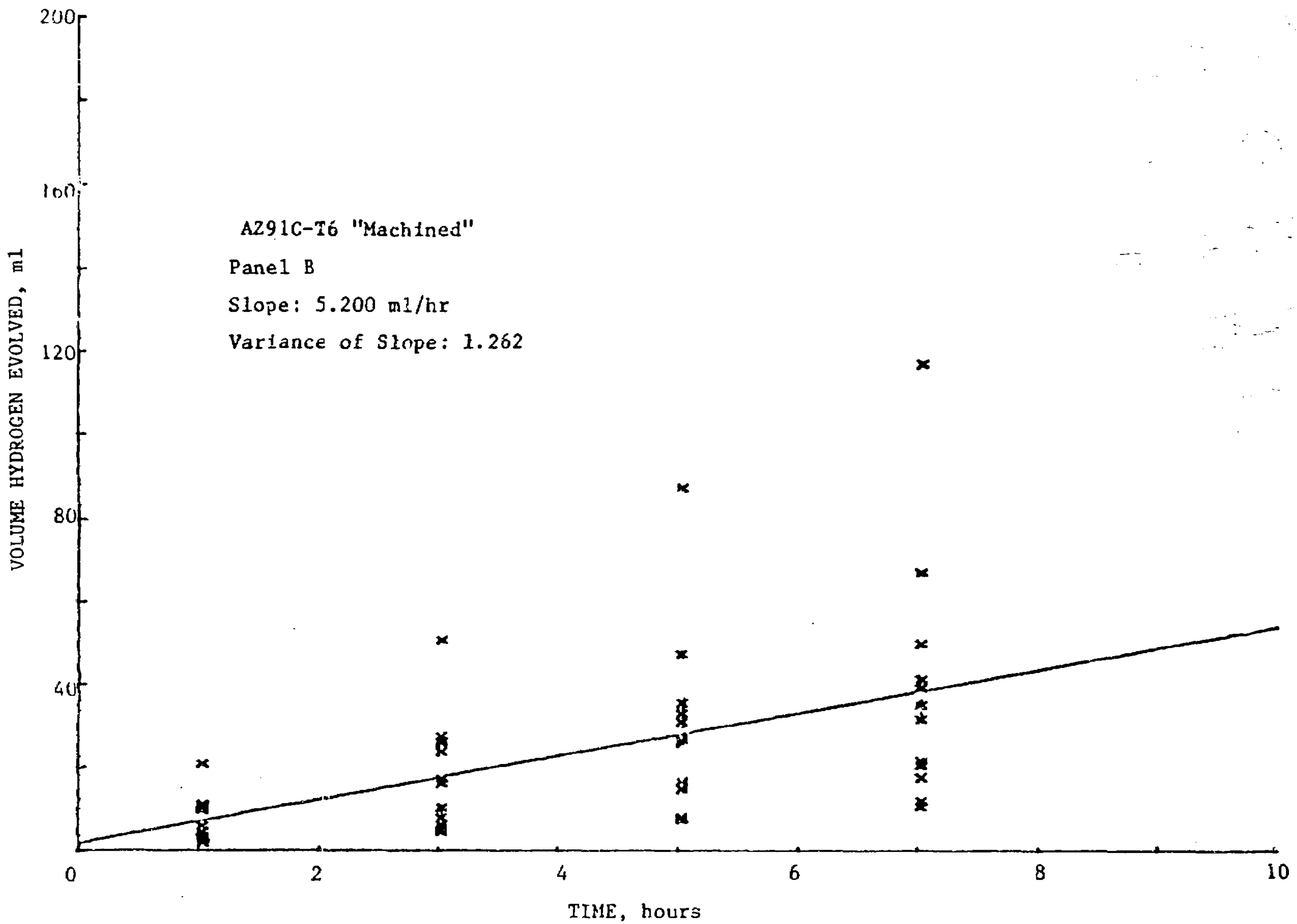

Figure 8. Hydrogen evolution, AZ91C-T6 machined, panel B

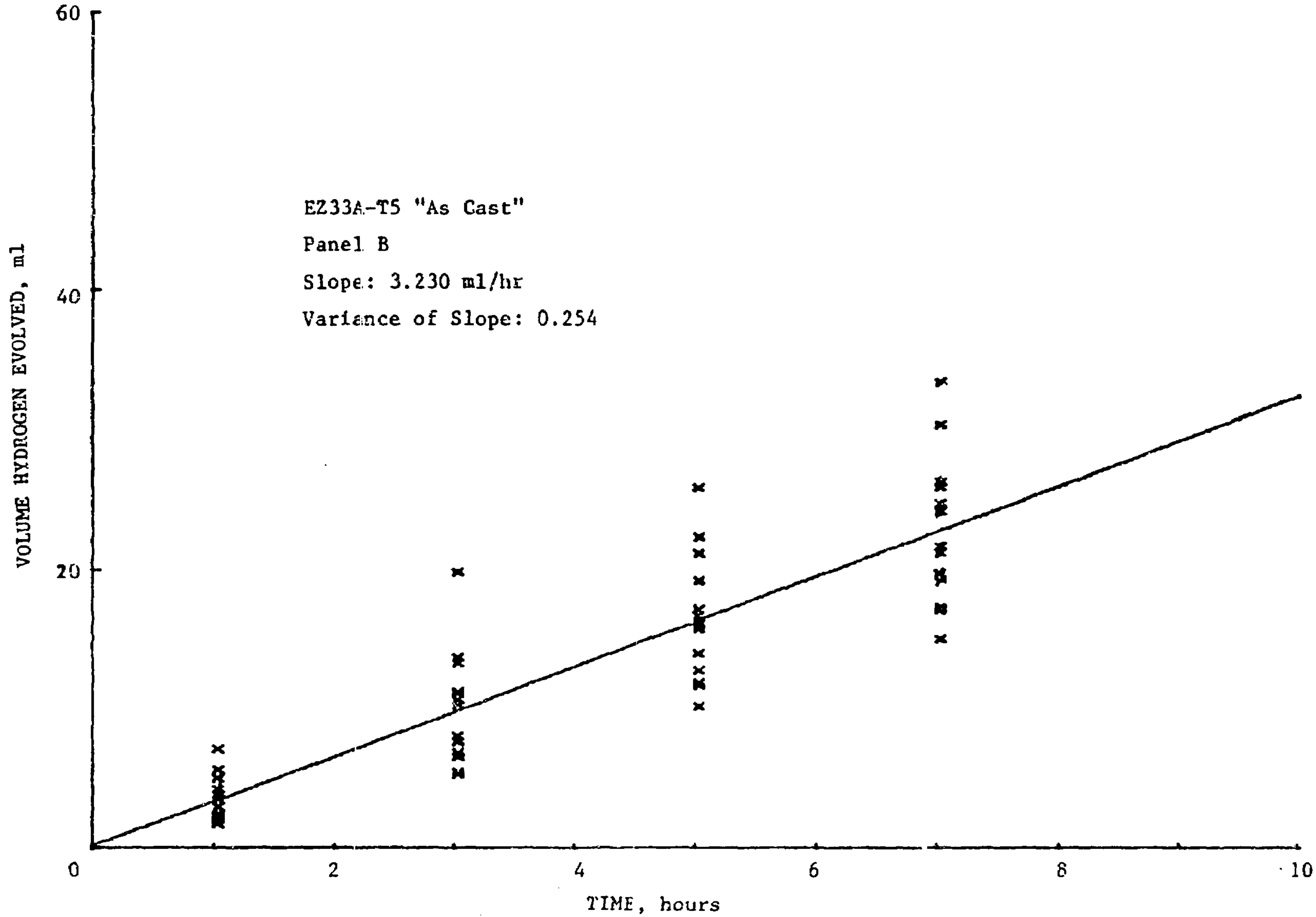

Figure 9. Hydrogen evolution, EZ33A-T5 as-cast, panel B

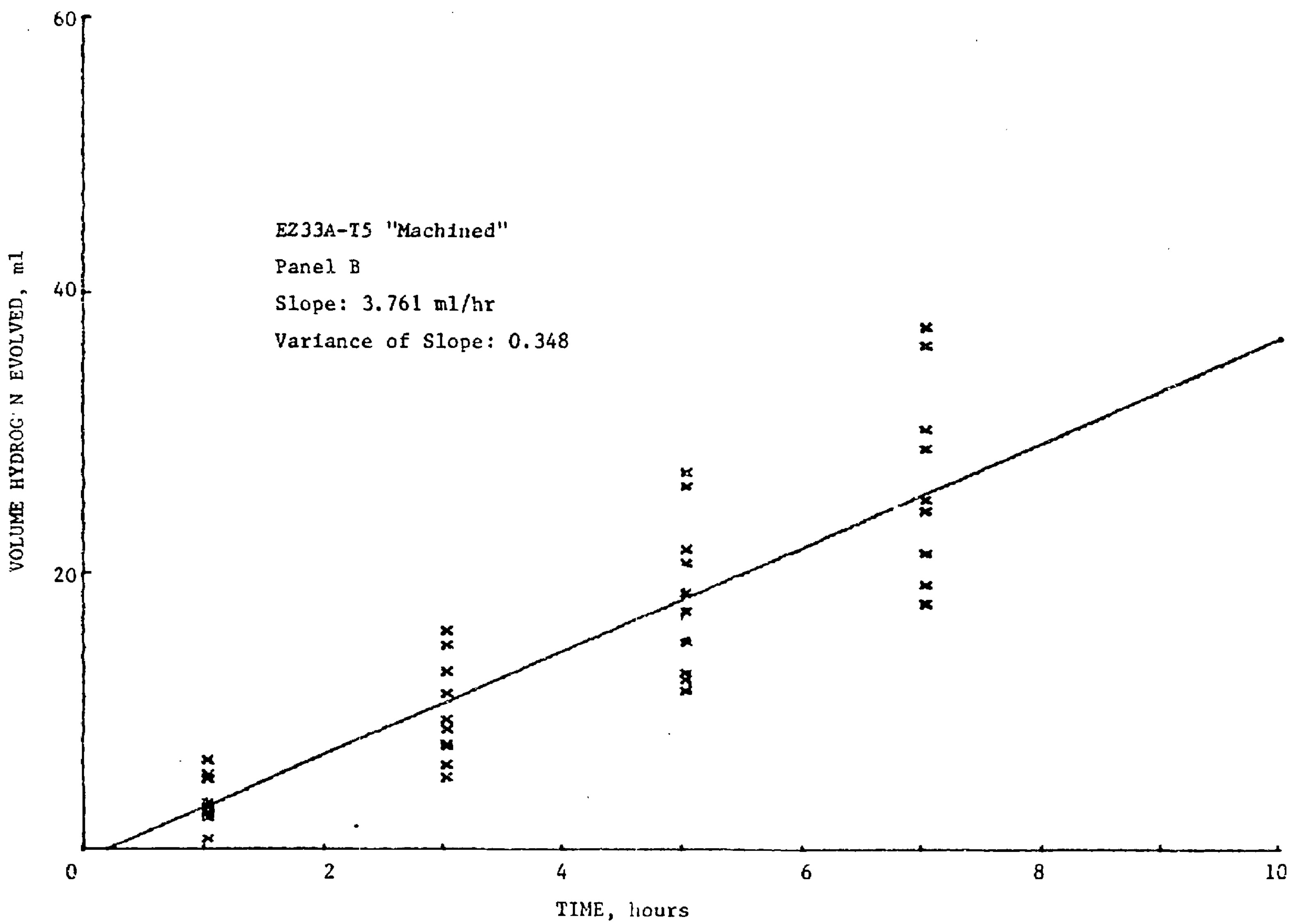

Figure 10. Hydrogen evolution, EZ33A-T5 machined, panel B

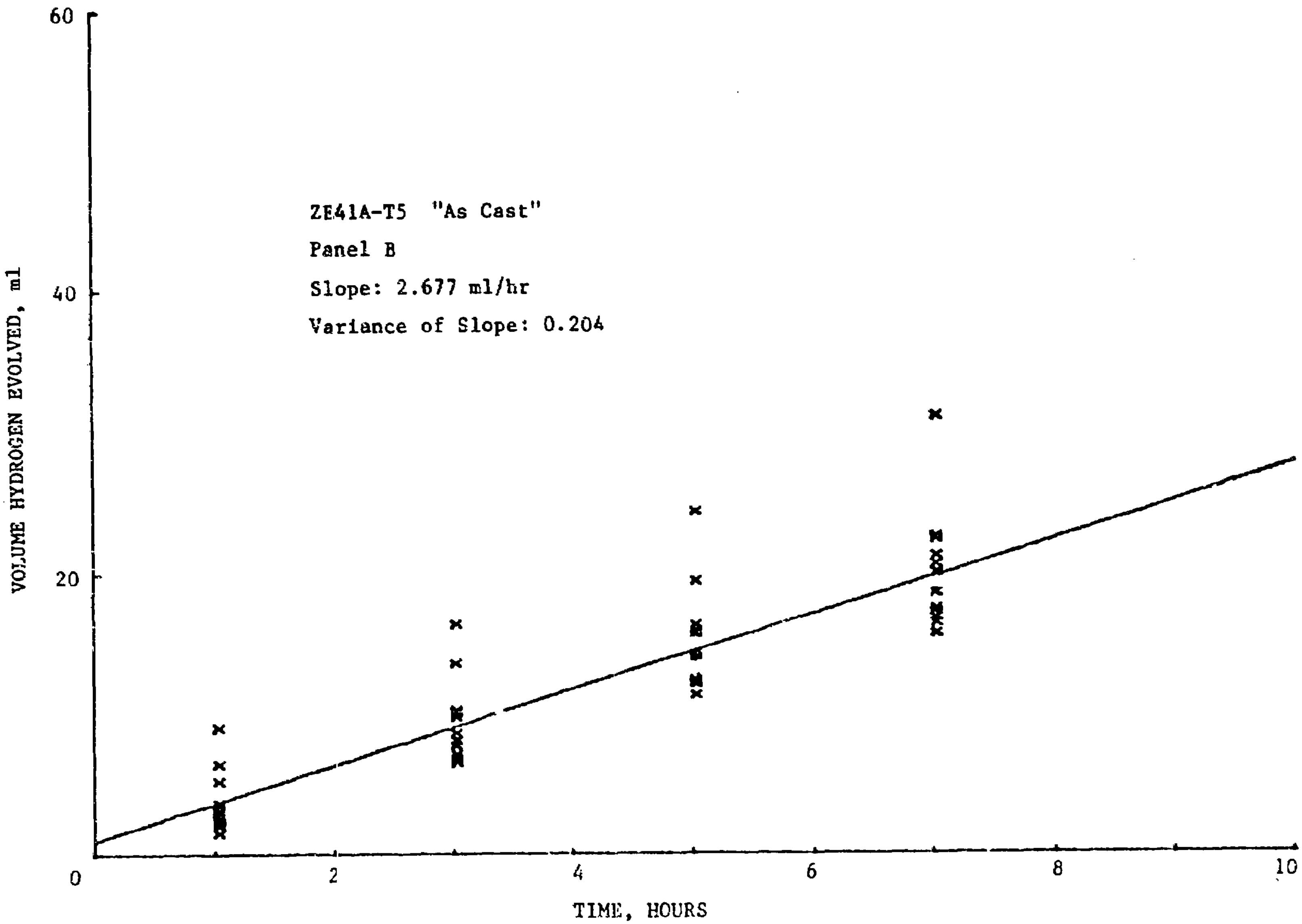

Figure 1'. Hydrogen evolution, ZE41A-T5 as-cast, panel B

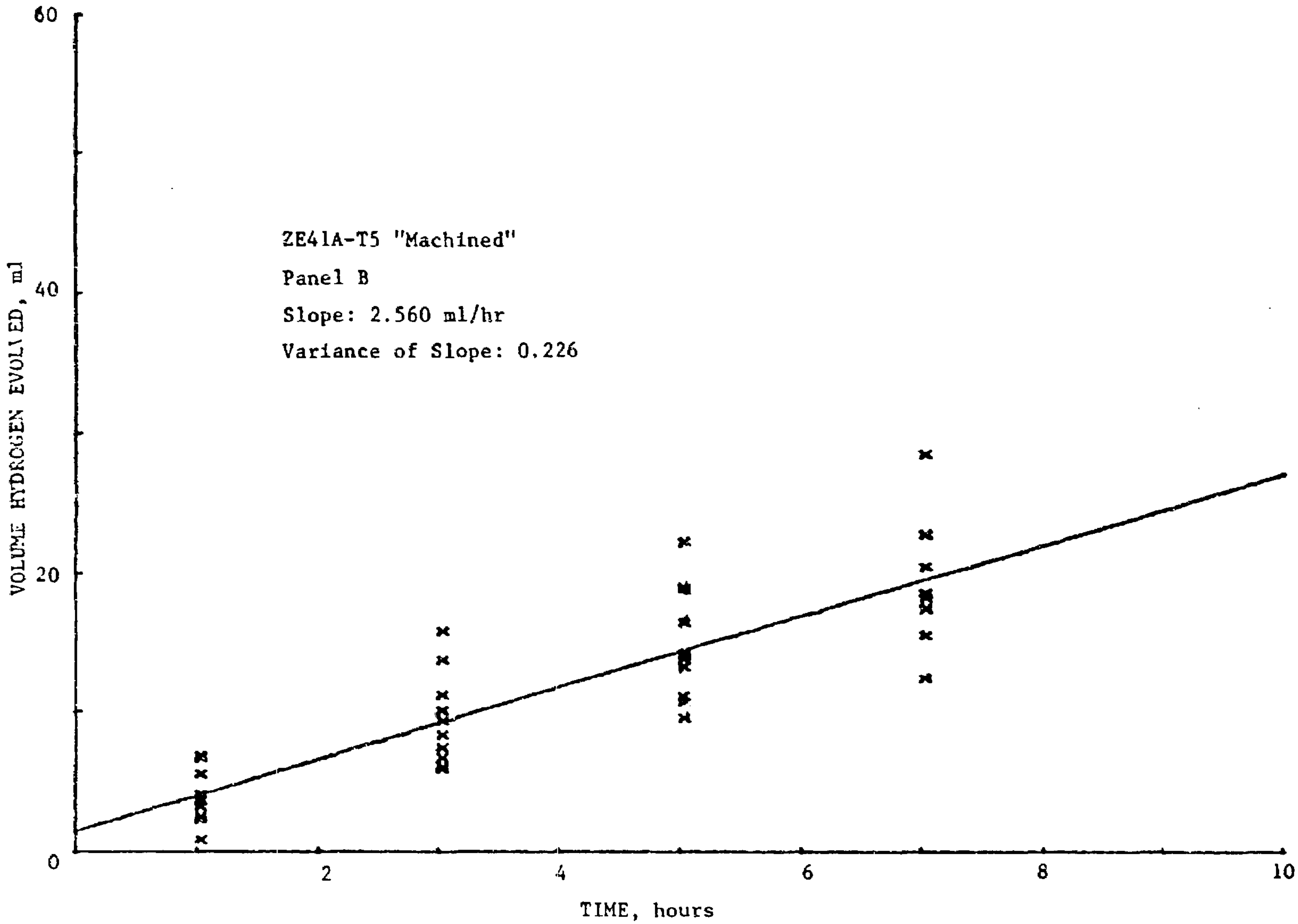

Figure 12. Hydrogen evolution, ZE41A-T5 machined, panel B

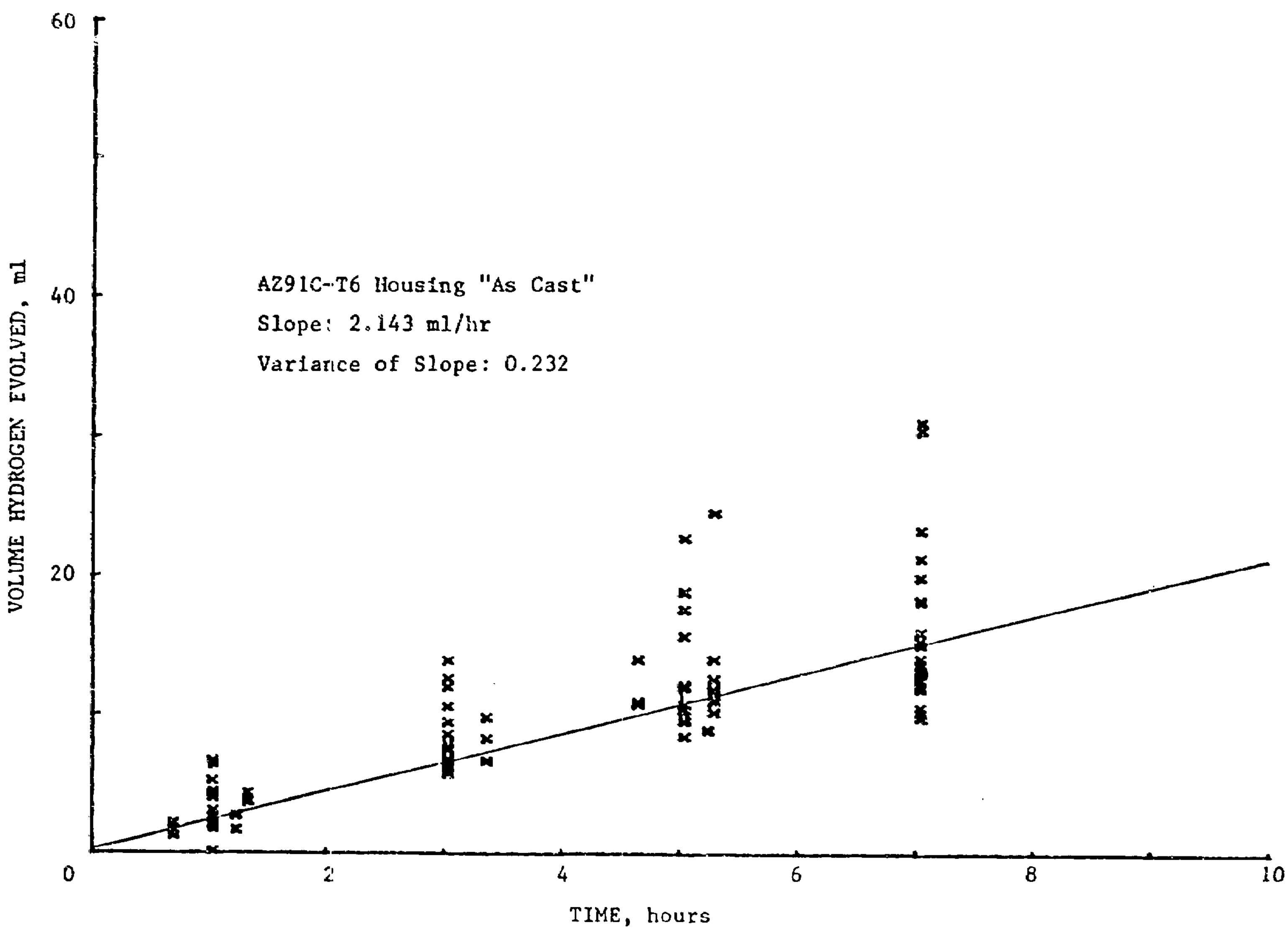

Figure 13. Hydrogen evolution, AZ91C-T6 housing as-cast

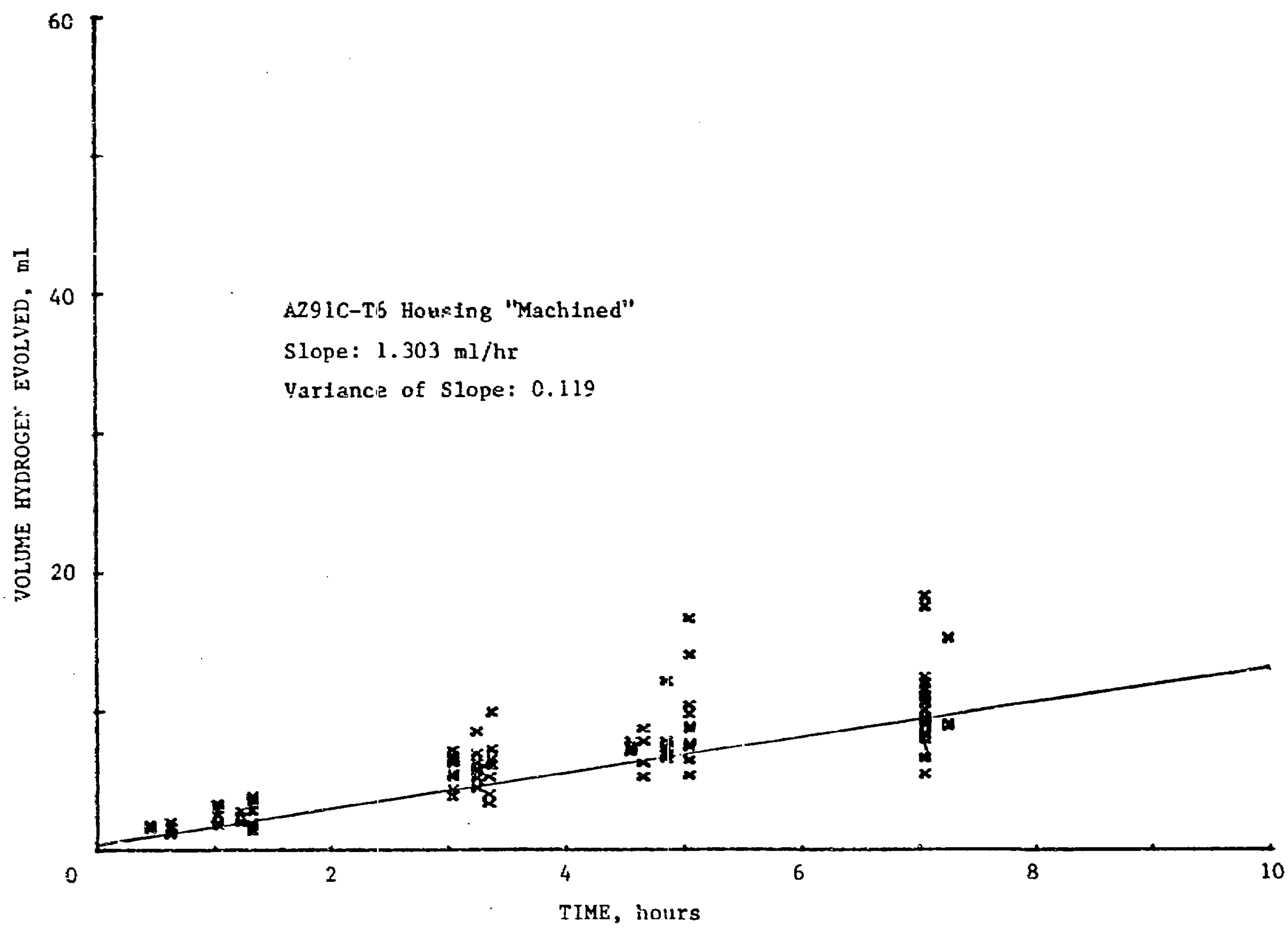

Figure 14. Hydrogen evolution, AZ91C-T6 housing machined

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